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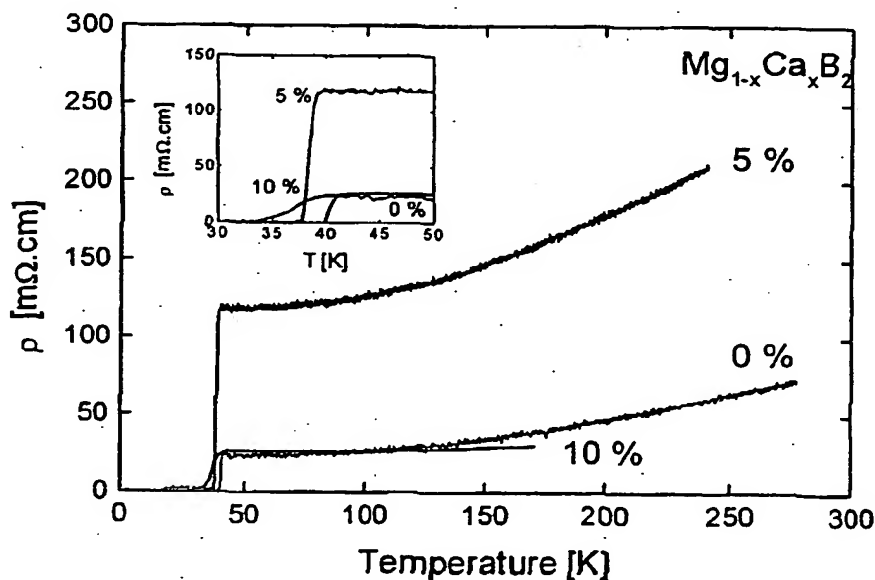
(57) Abstract: The invention comprises superconducting materials comprising metal borides of chemical formula $Mg_{1-x}X_xB_2$, where $0<x\leq0.5$ and X is Ca, Be, Al, Li, Zn, Cu, Ni, Cr, Ti, Zr, Gd or any combination thereof, which exhibit superconductivity at temperatures exceeding 30K. The invention includes superconducting wires made from $Mg_{1-x}X_xB_2$ where $0\leq x\leq0.5$ which may be made using the "powder-in-tube" method whereby precursor powders for $Mg_{1-x}X_xB_2$ are inserted into a metallic tube, which may then be subjected to a series of mechanical and thermal treatments to densify and react the boride superconductor and thereby provide superconducting wire. The boride precursor may be separated from the metal of the tube using an inert spacer material such as boron nitride. Such wires may be rebundled one or more times to provide a multifilamentary superconducting wire.

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SUPERCONDUCTING BORIDES AND WIRES MADE THEREOF

FIELD OF THE INVENTION

The invention relates to $Mg_{1-x}X_xB_2$, superconductors, and methods of forming conductors in which the superconductive material is of this compound or composition.

BACKGROUND

Superconductors are known to have application in magnets, cables, motors, generators, transformers and other related devices and technologies. Once cooled below their critical temperature, T_c, superconductors lose their resistance to DC electrical current and hence conduct electricity efficiently and may carry a very high electrical current density. These remarkable properties motivate the aforementioned commercial and scientific applications. Examples of such superconductors which have been used in such applications include niobium tin and niobium titanium. These have low T_c values and are generally referred to as low-temperature superconductors (LTS). The discovery of high-temperature superconductor (HTS) materials based on cuprate oxides with T_c values exceeding the boiling point of liquid nitrogen (77K) raised the prospect of wider scale application because of their potential use at more easily accessible temperatures.

The common method for preparing long-length HTS wires is the so-called powder-in-tube method whereby precursor powders are packed into a metal tube, usually silver, which is then drawn down in size, then several of these drawn wires may be bundled together in another metal tube, usually silver, which is then subjected to a series of rolling and heat treatment steps. This results in a thin HTS tape with multiple filaments. The drawn wire may be rebundled more than once to achieve higher numbers of filaments. Filamentary wires are particularly useful for AC applications because of the need to reduce AC losses which are known to be diminished through the division of a superconductor into filaments. However, of all the known HTS cuprates only two, generally referred to as $Bi_2Sr_2CaCu_2O_{8+\delta}$ and $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$, are amenable to the powder-in-tube technique. The obstacle is that polycrystalline HTS materials must (1) be aligned so that their grains have a common c-axis alignment and (2) be densified so that grain boundaries are atomically smooth. The aforementioned bismuth based HTS cuprates have a micaceous

5   morphology that causes their grains to be aligned in the process of the deformation of the
containing metal tube. The grains also have an operative slip system that allows them to
densify and achieve atomically-smooth grain boundaries. This is essential because the HTS
cuprates have a very short coherence length, often less than 1.8nm, which results in weak
links between grains that have grain boundary disorder extending over a distance
10   comparable to 1.8nm. As noted no other HTS cuprate possess this ability under
deformation to densify, align and develop smooth grain boundaries. However, these HTS
bismuth cuprates happen to have very weak pinning such that they cannot sustain large
critical currents in the presence of a magnetic field. As a consequence HTS cuprates are in
general very limited in their application in the form of superconducting wires and tapes.

15

SUMMARY OF THE INVENTION

The present invention provides for superconducting materials which have a long coherence
length and therefore minimise the limitations discussed above relating to weak links
20   between grains.

In one aspect the invention comprises a superconductor which exhibits superconductivity
at a temperature exceeding 30K, of chemical formula or composition $Mg_{1-x}X_xB_2$, where
$0<x\leq0.5$ and X is Ca, Be, Al, Li, Zn, Cu, Ni Cr, Ti, Zr, Gd, W, Mo or any combination
25   thereof.

In another aspect the invention comprises an elongate superconductive electrical conductor
comprising a superconductor of chemical formula or composition $Mg_{1-x}X_xB_2$, where
$0\leq x\leq0.5$ and X is Ca, Be, Al, Li Zn, Cu, Ni Cr, Ti, Zr, Gd, W, Mo, or any combination
30   thereof.

Preferably $0<x\leq0.3$. More preferably $0<x<0.1$. Most preferably $0<x<0.08$.

Preferably X is Al, Cu, Zn or a combination thereof.

35

5   In a further aspect the invention comprises a method of forming an electrical conductor including compacting within an elongate metal container particles of a superconductor of chemical formula or composition $Mg_{1-x}X_xB_2$, where $0 \leq x \leq 0.5$ and X is Ca, Be, Al, Li Zn, Cu, Ni Cr, Ti, Zr, Gd, W, or Mo, or any combination thereof.

10   Preferably the method includes mixing together and reacting precursor materials to form a superconductor of chemical formula or composition $Mg_{1-x}X_xB_2$, where $0 \leq x \leq 0.5$ and X is Ca, Be, Al, Li Zn, Cu, Ni Cr, Ti, Zr, Gd, W, Mo, or any combination thereof.

Preferably the method includes intimately mixing particles of the precursor materials and
15   compacting the precursor materials into and reacting the precursor materials in an elongate metal container.

Preferably the precursor materials include elemental boron and elemental magnesium.

20   Preferably the method includes heating the precursor materials to a reaction temperature sufficient to vaporize the magnesium precursor to react with the boron precursor in a gas-solid reaction.

Preferably the method includes providing an inert layer between the superconductor
25   compound or precursor materials and the interior surface of the metal container.

Preferably the inert layer is a layer of boron nitride.

Preferably the method includes placing the precursor materials within the elongate metal
30   container such that the boron precursor material is substantially surrounded by the magnesium precursor material.

Preferably the method includes heating to react the precursor materials to a temperature between about 400°C and about 950°C.

5   Preferably the method includes intimately mixing the precursor materials as particles of average particle size less than one micron prior to heating and reacting the precursor materials.

Preferably the method includes mixing the precursor materials together so as to form an alloy of precursor metals. Preferably the method includes then heating and reacting the

10   precursor materials at a temperature in the range about 400°C to about 750°C.

Preferably the method includes subjecting the elongate metal container containing the precursor materials or an elongate component formed of an alloy of the precursor materials

15   to mechanical deformation to densify the precursor material.

Preferably the mechanical deformation includes further elongating the metal container or alloy component to reduce the cross-sectional dimension thereof and further compact the material therein.

20

Preferably the method includes also heating the metal container or alloy component while subjecting it to mechanical deformation to assist in densifying the material.

Preferably the method includes carrying out a heat treatment of the superconductor to

25   precipitate borides of the substituent metal X from the superconductor.

Preferably the method includes heating to sinter particles of the superconductor together.

The invention also includes a method of forming an electrical conductor including the

30   steps of : intimately mixing at the sub-micron level particles of a magnesium precursor material and a boron precursor material and a precursor material which is a source of Ca, Be, AL, Li, Zn, CU, Ni, Cr, Ti, ZR, Gd, W, Mo or any combination thereof, compacting the precursor materials within an elongate metal tube, subjecting the metal tube to mechanical deformation to reduce the cross-sectional dimension thereof and further

35   compact the materials therein, and heating the metal container to react the precursor materials to form a superconductor of chemical formula or composition $Mg_{1-x}X_xB_2$, where

5      $0 \leq x \leq 0.5$ and X is Ca, Be, Al, Li Zn, Cu, Ni Cr, Ti, Zr, Gd, W, or Mo, or any combination
       thereof, where x is between $0 \leq x \leq 0.5$ and to precipitate fluxpinning – effective borides of
       the substituent metal X distributed within the resultant superconductor material.

       The invention also includes a method of forming an electrical conductor including the
10   steps of : intimately mixing at the sub-micron level particles of a magnesium precursor
       material and a boron precursor material and a precursor material which is a source of Ca,
       Be, AL, Li, Zn, CU, Ni, Cr, Ti, ZR, Gd, W, Mo or any combination thereof, subjecting the
       elongate alloy component to mechanical deformation to reduce the cross-sectional
       dimension thereof, and heating the alloy component to react the precursor materials to
15   form a superconductor of chemical formula or composition $Mg_{1-x}X_xB_2$, where $0 \leq x \leq 0.5$
       and X is Ca, Be, Al, Li Zn, Cu, Ni Cr, Ti, Zr, Gd, W, or Mo, or any combination thereof,
       where x is between $0 \leq x \leq 0.5$ and to precipitate fluxpinning – effective borides of the
       substituent metal X distributed within the resultant superconductor material.

20   **BRIEF DESCRIPTION OF THE FIGURES**

       The invention is further illustrated by the following examples and is described with
       reference to the accompanying figures in which:

25   Figure 1 is a schematic diagram of the cross-section of a conductor comprising a metal
       tube and precursor to the boride superconductor.

       Figures 2A and 2B are schematic diagrams of the cross-section of flat or tape conductors
       comprising a metal tube and precursor to the boride superconductor.
30

       Figure 3 is a schematic diagram of the cross-section of an approximately circular
       conductor comprising a metal tube, boron or the precursor to the material $Mg_{1-x}X_xB_2$ and
       optional metal tube comprising predominantly magnesium and an inert spacer layer which
       protects the metal tube from reaction with the superconductor precursor.

35

5   Figure 4 is a schematic diagram of the cross-section of an approximately circular
        multifilamentary conductor comprising a metal tube, containing individual wire filaments
        which may be the wires or Figure 1 or of Figure 3 an alternative layout using flat tapes
        such as those shown in Figure 2 as flat filaments could be used.

10   Figure 5 is a plot of the resistivity for samples of composition $Mg_{1-x}Ca_xB_2$ with x= 0, 0.05
        and 0.10. (the last sample is multiphase).

        Figure 6 is a plot of the resistivity for samples of nominal composition $Mg_{1-x}Ni_xB_2$ with x=
        0, 0.03, 0.05 and 0.08.

15

        Figure 7 is a plot of the resistivity for samples of composition $Mg_{1-x}Zn_xB_2$ with x= 0, and
        0.05.

        Figure 8 is a plot of the resistivity of the face of MgB_2 material that had been reacted in a
20   stainless steel tube at 900°C. The face of the material was adjacent to the stainless steel and
        shows no degradation of T_c.

        Figure 9 is a plot of the resistivity for samples of composition $Mg_{1-x}Cu_xB_2$ with x= 0, 0.10
        and 0.20.

25

        Figure 10 shows 12 x-ray diffraction traces for the cores of alloyed magnesium-boron
        material reacted at the temperatures and duration shows for each trace. The upper trace
        shows the pattern for the precursor magnesium-boron material and the bottom trace shows
        the pattern for a conventional ceramic pellet sample reacted at 900°C. In all cases reactions
30   were carried out in an atmosphere of 5% H_2 and 95% argon.

        Figure 11 shows a plot of critical current density, J_c, as a function of applied magnetic field
        for an alloyed sample reacted for two hours at 600°C.

5

DETAILED DESCRIPTION

In a preferred form of the invention the precursors to the superconducting boride
compositions are placed in a metal tube. The precursor materials may be in the form of
10   elemental magnesium mixed in stoichiometric proportion with elemental boron, preferably
amorphous boron, together with the substituent X in elemental form. The mixing of the
precursor powders may be simple mechanical mixing, as in stirring, or by milling or any
other known form of mixing. We have found the reaction of the elemental precursors to be
remarkably uniform in spite of poor mixing where, at the temperature of synthesis, the
15   magnesium vaporises and reacts with the boron as a gas solid reaction. The metal tube is
then preferably drawn, extruded or otherwise deformed so as to reduce its cross-sectional
area to effectively densify and further compact the introduced precursor material. This
simple geometry is illustrated in Figure 1 where 1 denotes the metal tube and 2 denotes the
precursor material. In general the cross-section need not be circular but may be hexagonal,
20   square, elliptic or any other suitable shape.

Figure 2 illustrates another approach in which the precursor materials are placed within the
encasing metal tube such that the boron precursor material is substantially surrounded by
the magnesium precursor material. This approach reduces or prevents reaction of the
25   precursor materials with the encasing metal tube 1. The material of the central core 4 may
be predominantly boron. The material 3 may be predominantly magnesium or $Mg_{1-x}X_x$.
preferably in the form of a metal tube. The material 2 may be an inert material such as
boron nitride, for example, which has the advantage of deformability when packed in a
tube which is to be drawn, extruded or subjected to other such deformations. We have
30   found boron nitride to not react appreciably with MgB_2 or related materials under typical
conditions of synthesis and reaction. Alternatively the layer 2 may be a suitable metal
which protects the outer tube 1 from reaction with the $Mg_{1-x}X_x$ material 3. This is
especially preferred if the outer metal is copper or stainless steel, for example. The metal 2
in Figure 3 may be nickel, aluminium, magnesium, chromium or silver and may be
35   inserted as a tube or coated on the inner surface of the outer metal 1. Such coating
techniques will be well known to practitioners of the art. Aluminium is particularly

5   preferred because it provides good electrical contact with the outer metal but if it should

        react with boron in the precursor material it forms AlB_2 which, while not superconducting,

        is a good conductive metal providing good electrical connection between the outer metal

        and the inner superconductor. If magnesium is used for the material 2 in Figure 3 then

        layer 3 may not be necessary and material 4 may be the $Mg_{1-x}X_xB_2$ precursor, with a

10   suitable deficiency of Mg to allow for source 3 of Mg. The precursors may be elemental

        magnesium, elemental boron, and elemental metal x for example.

        Figure 2A is similar to Figure 1. Outer tube 1 contains mixed precursor materials 2, or

        alternatively pre-reacted $Mg_{1-x}X_xB_2$ material compacted into the outer tube 1. Figure 2A

15   is similar to Figure 3 except that the conductor is in the form of a flat tape, comprising a

        metal tube 3 a boride precursor 6, a magnesium precursor 4 as a tube, and an inert layer 5

        between the precursor materials and the interior of the outer tube 3.

        The outer container or tube 1 in Figure 1, Figure 2 or Figure 3, may be silver, gold, copper,

20   nickel, a so-called stainless steel, or any other common metal or alloy, typically with

        melting point in excess of 900°C.

        Following deformation of the packed metal tube, such as by extrusion, drawing, swaging

        or other such like deformations, then the resultant tube or wire may be bundled with other

25   similarly produced tubes or wires, inserted in another metal tube and redeformed to

        produce a multicored or multifilamentary conductor as illustrated in Figure 4 where, for

        example, seven such filaments have been bundled. The choice of the number of such

        filaments is not restricted and such choice will be made on the basis of manufacturing

        convenience. The individual wires making up the multifilamentary conductor of Figure 4

30   may be the wires of Figure 1 or the heterogeneous wires of Figure 3. The detail of the

        cross-sections of the individual filaments in Figure 4 is not shown but should be

        understood to generally represent either a cross-sectional structure as in Figure 1 or in

        Figure 3.

35   Heat treatment of the aforementioned wires, tapes, or multifilamentary conductors in order

        to react the precursor superconductor materials involves heating at temperatures exceeding

5   780°C, preferably 850-950 °C, for duration exceeding 10 minutes and preferably 1-4 hours, in an inert atmosphere such as nitrogen, argon, hydrogen or any combination thereof, but preferably argon and most preferably argon mixed with hydrogen. The wires, tapes or conductors may be raised quickly or slowly to the reaction temperature and may be cooled quickly or slowly back to room temperature.

10

Preparation of such materials, wires or tapes may be carried out in a preferred form by milling together stoichiometric quantities of Mg, X and B metals in an inert atmosphere until the precursor metals are intimately mixed at the sub-micron level eg having an average particle size less than one micron, and preferably at the nanometer level as in

15   alloying. This intimately mixed material is found to be more reactive than mixed powders as described above. Such milling may form an alloy of the Mg, X and B metals. The intimately mixed or alloyed materials are then reacted as bulk material or introduced into a metal tube or billet so as to extrude or draw down the tube to a smaller diameter and then make a single or multiple filament wire according to methods known in the art and as

20   described above. Such bulk material or wire then is found to react in an inert atmosphere or a reducing atmosphere such as H_2, or H_2 mixed with an inert atmosphere, for example, at a temperature between 750°C and 850°C for a time between 10 minutes and 6 hours. The outcome of such intimate mixing is that the reaction proceeds at a lower temperature than otherwise is achieved. In a wire or tape technology such lower temperature reaction is

25   desirable to minimise reaction with the metal of the cladding tube and the metal matrix surrounding the filaments. The smaller is the length scale of the mixing the lower the temperature of reaction needs to be and/or the shorter the reaction time. It is preferred that the mixing be on the nanometer scale thus allowing reaction temperatures between 750°C at 850°C, for example.

30

As a specific and preferred form of milling to achieve intimate nanoscale mixing, stoichiometric quantities of Mg, X and B metals may be milled in an inert atmosphere until the precursor metals are alloyed. This alloyed material is found to be very reactive and is found to be more dense than mixed and compressed powders (which may be as low as

35   40% of theoretical density). The alloyed materials are then reacted as bulk material or introduced into a metal tube or billet so as to extrude or draw down the tube to a smaller

5   diameter and then make a single or multiple filament wire according to methods known in
     the art and as described above.. Such bulk material or wire then is found to react in an inert
     atmosphere or a reducing atmosphere such as H_2, or H_2 mixed with an inert atmosphere,
     for example, at a temperature between 400°C and 850°C for a time between 10 minutes
     and 48 hours, for example. The outcome of such alloying is that the reaction proceeds at a

10   very much lower temperature than otherwise is achieved. In a wire or tape technology such
     lower temperature reaction is desirable to minimise reaction with the metal of the cladding
     tube and the metal matrix surrounding the filaments. By such alloying reaction
     temperatures may be as low as 400°C, for example and such low temperatures preferably
     allow the use of copper metal, for example, as the cladding or matrix material. Under usual

15   circumstances copper metal is not a suitable cladding material as it reacts with magnesium
     at high temperatures. This reaction is strongly enhanced above the melting point 651°C of
     magnesium metal. Reducing the reaction temperature even further to below the 485°C
     eutectic point of the Cu-Mg phase diagram could further reduce or eliminate alloying of
     Cu and Mg.

20

     Flux pinning vortices may be introduced into in the novel materials $Mg_{1-x}X_xB_2$ so as to
     provide for enhanced critical currents. We have observed that several substituents, X,
     exhibit a solid solubility up to a critical fraction, x. It is further the case that the presence
     of a small volume, particle, precipitate or other such inclusions of non-superconducting

25   material causes flux lines to preferentially bind to said inclusions thus providing pinning of
     flux lines and consequent increase in critical current density, J_c. It is most desirable to
     increase J_c in superconductors. Such inclusions or precipitates may be incorporated into
     the structure of MgB_2 or of $Mg_{1-x}X_xB_2$ by heat treatment between 400-450°C and 950°C so
     as to precipitate out the boride or borides of X. Preferred substituents, X, to provide for

30   such precipitates include Al, Cu, Zn, Ni, Fe, Cr, Ti, Zr, Gd, W or Mo. Especially preferred
     substituents for causing flux pinning precipitates include Al, especially in concentrations
     $0.1 \leq Al/Mg \leq 0.3$. Preparation of such materials with flux pinning precipitates may be
     carried out in preferred form by milling together Mg, X (=Al, for example) and B metals in
     an inert atmosphere until the precursor metals are intimately mixed at the sub-micron level

35   and preferably at the nanometer level or alloyed. This intimately mixed or alloyed material
     may then be reacted as bulk material or introduced into a tube or billet so as to extrude or

5   draw down the tube to a smaller diameter and then make a single or multiple filament wire
       according to methods known in the art and as described above. Such bulk material or wire
       may then be reacted in an inert atmosphere or a reducing atmosphere such as H_2, or H_2
       mixed with an inert atmosphere, for example, at a temperature between 450°C or 950°C
       for a time between 10 minutes and 48 hours, for example, both to react to form the active
10   superconductor but also to form the flux-pinning precipitates. In general a different heat
       treatment may be used to carry out the reaction and to carry out the flux-pinning
       precipitation. The smaller is the length scale of the mixing the lower the temperature of
       reaction needs to be and/or the shorter the reaction time. It is preferred that the mixing or
       alloying be on the nanometer scale thus allowing reaction temperatures between 750°C
15   and 850°C and even as low as 400°C, for example, with the result that the precipitates
       (such as AlB_2, for example) do not grow to a large size, greater than 1 μm for example. It
       is preferred that the size of the precipitates lies between 4 and 100nm.

       Example 1
20   A range of calcium-substituted magnesium boride compounds of formula $Mg_{1-x}Ca_xB_2$ x=0,
       0.05 and 0.10 were synthesised by reacting a 20 millimole stoichiometric mixture of (1-
       x)Mg, xCaO, xC and 2B under H_2 gas for 1 hour at 900°C after ramping to this
       temperature over 1.5 hours. The presence of the carbon is necessary to carbothermally
       reduce the CaO. The powders were mixed, milled and die pressed into 12mm diameter
25   pellets. These were placed in an alumina crucible lined with tantalum metal. The pellets
       were capped with a sheet of tantalum then boron nitride powder was used to fill the
       remainder of the crucible to reduce the evolution of magnesium vapour. X-ray diffraction
       showed that the x=0 and x=0.05 samples were essentially single phase while other phases
       such as MgO and calcium boride appeared in the x=0.10 sample. The resistivity is plotted
30   as a function of temperature in Figure 5. This shows a superconducting transition
       temperature for the x=0 sample of just over 40K and a uniform reduction in T_c to 38.5K
       for the x=0.05 sample. The x=0.10 sample shows evidence in its transition of its mixed
       phase state.

35

5   **Example 2**

Samples of nickel- and zinc-substituted magnesium boride compounds of formula $Mg_{1-x}Ni_xB_2$ x=0, 0.03, 0.05 and 0.08 and $Mg_{1-x}Zn_xB_2$ x=0 and 0.05 were synthesised by reacting a 20 millimole stoichiometric mixture of (1-x)Mg, 2B and xNi or xZn powders under H_2 gas for 1 hour at 920°C after ramping to this temperature over 1.5 hours. The

10   powders were mixed, milled and die pressed into 12mm diameter pellets. These were placed in an alumina crucible lined with tantalum metal. The pellets were capped with a sheet of tantalum then boron nitride powder was used to fill the remainder of the crucible to reduce the evolution of magnesium vapour. X-ray diffraction showed that only the MgB_2 and $Mg_{1.95}Zn_{0.05}B_2$ samples were single phase while other impurity phases were

15   present in the Ni samples. The resistivity for the Ni-substituted samples is plotted as a function of temperature in Figure 6. This shows a superconducting transition temperature for the x=0 sample of just over 40K and a uniform but very slow reduction in T_c to 39K for the x=0.08 sample. In spite of the presence of a small amount of impurity the resistivity remains very low and the T_c values hardly change. This means that magnesium boride will

20   survive synthesis in a nickel tube and still display strong intergranular links and a relatively unchanged transition temperature. The slow reduction in transition temperature is probably associated with a small fraction of Ni substituting into the MgB_2 and acting as a magnetic pairbreaker. In contrast the effect of Zn which appears to have substituted fully into the MgB_2 structure is a very minor reduction in T_c consistent with the absence of a magnetic

25   moment in the Zn atom and hence the absence of magnetic pairbreaking. This suggests that the symmetry of the order parameter is s-wave. The element Be can also be substituted into MgB_2 according to the chemical formula $Mg_{1-x}Be_xB_2$ with $0 \leq x \leq 0.5$ using much the same method as described above for Ni and Zn. However because of the toxicity of Be especially the oxide of beryllium it is necessary to take several precautions. Be wire is cut

30   into short lengths and mixed with the Mg and B precursor and the mixture pressed into a pellet. The pellet is then placed on a tantalum foil and sealed in a quartz ampoule under argon gas at 0.5 atmosphere by fusing the quartz. This is then placed in a stainless steel container which is then placed in a tube furnace under a strong flow of nitrogen gas and reacted for 1 hour at 900°C after heating to this temperature over 1.5 hours.

35

5   **Example 3**

A well mixed stoichiometric powder mixture of Mg and B was loaded into a copper tube which was then drawn down in diameter with intermittent anneals for 1 hour at 250°C in air to eliminate the work hardening of the copper. The resultant copper-clad wire was then cut into sections and several of these were reacted for 1 hour at 900°C under flowing

10   hydrogen gas. The resistivity of the wire was measured and found to display a sharp superconducting transition at 40K similar to the bulk pellets described above. The surface of the MgB_2 in contact with the copper metal was then exposed. It showed some discolouration. A four terminal resistivity measurement was made on the surface exposed to the copper metal and this exhibited a very low resistivity in the normal state similar to

15   the pure material and a good sharp transition at 40K.

Example 4

A well mixed stoichiometric powder mixture of Mg and B was loaded into a silver tube which was then drawn down in diameter to about 1.5mm diameter with intermittent

20   anneals for 1 hour at 250°C in air to eliminate the work hardening of the silver. The resultant silver-clad wire was then cut into sections and several of these were reacted for 1 hour at 900°C under flowing hydrogen gas. The resistivity of the wire was then measured and found to display a sharp superconducting transition at 40K similar to the bulk pellets described above.

25

Example 5

A well mixed stoichiometric powder mixture of Mg and B was loaded into a 316 stainless steel tube. This tube was then reacted for 1 hour at 900°C under flowing hydrogen gas. The resistivity of the wire was then measured and found to display a sharp superconducting

30   transition at 40K similar to the bulk pellets described above. A piece of 316 stainless steel foil was placed in a 12mm die on top of a stoichiometric precurser mixture of Mg + 2B. More precursor mixture was placed on top, the powder levelled and the piston inserted. A pellet was pressed with the stainless steel fully contained therein. The pellet was reacted in flowing H2 gas as above by heating to 920°C over 1.5 hours then reacting at 920°C for 1

35   hour. After cooling the pellet was then opened to expose the faces that juxtaposed the stainless steel. There was some discolouration evident. A four terminal measurement of the

5   resistivity of the surface of the pellet adjacent to the stainless steel is shown in Figure 8. It
       shows a typical low resistivity and a good sharp transition at 40K, indeed the onset of the
       transition is slightly higher than for the pure compound by 1.4K.

       Example 6
10   Stoichiometric precursor Mg + 2B powder was loaded into a copper tube lined with a thin
       wall of aluminium and processed as in example 4 with similar results.

       Example 7
       High purity elemental magnesium and boron were mixed in the stoichiometric proportions
15   of MgB_2. The charge of material was then mechanically milled for 6 hours under an
       atmosphere of argon gas. The resultant material was packed into a copper billet which was
       then evacuated prior to extrusion. The billet was hot and extruded at 200°C to form a wire.
       The extruded wire was then drawn down in diameter to an external hexagonal cross-
       section of 3.6 mm across the flats and a cylindrical internal cross-section of 2.4mm
20   diameter containing the densely-packed alloyed magnesium-boron material. The wire was
       cut into lengths of 20 to 30 mm and some had the copper cladding removed mechanically
       in a lathe, so that the reaction could be studied independently of the copper sheath.

       The short-length samples were reacted in an atmosphere of 5% H_2 and 95% argon for
25   periods of time ranging from 10 minutes to 24 hours. It was generally found that when the
       alloyed materials were reacted under similar conditions to conventional pellets and wires
       as described in examples 1 to 6 above, namely around 900°C, the magnesium-boron
       material did not react to the desired MgB_2 phase but to MgB_4. Lower temperatures,
       however, resulted in successful synthesis of MgB_2. Figure 10 summarises the results of this
30   example in the form of x-ray diffraction patterns obtained from exposed cores of the wires
       after reaction. The conditions of temperature and time of reaction are listed for each
       diffraction trace. The diffraction pattern at the top is for the precursor magnesium-boron
       alloyed material while the diffraction pattern for a conventional single phase MgB_2 pellet
       is shown at the bottom. The second trace shows that after just two hours at 500°C about
35   half of the material has reacted through to MgB_2 while the fifth trace shows that after 24

5   hours at 500°C the material has fully reacted to MgB_2. As a first advantage, this sample
       showed very little reaction with the copper cladding material. As a second advantage, the
       incorporation of aluminium, or some other element X, in the composition $Mg_{1-x}Al_xB_2$ with
       concentrations $0.1 \leq Al/Mg \leq 0.3$ will allow the formation of very fine precipitates of
       aluminium boride when reacted at temperatures as low as 500°C. Such very fine
10   precipitates will provide for enhanced flux pinning in MgB_2.

       A further short-length sample was reacted in an atmosphere of 5% H_2 and 95% argon for a
       period of 2 hours. The sample was then investigated in a vibrating-sample magnetometer
       to determine the magnetisation as a function of temperature and magnetic field strength.
15   Using the Bean critical state model and an established numerical fitting procedure the
       critical current density was determined from this magnetic data. Figure 11 shows the
       critical current density, J_c, plotted as a function of applied field for various temperatures.
       The results indicate a J_c value of 7×10^5 A/cm^2 at 14 K and zero applied magnetic field
       and 1×10^5 A/cm^2 at 20 K and 1 Tesla field. These are significantly better results than
20   those obtained for pressed, sintered pellets.

5   CLAIM:

1.   A superconductor which exhibits superconductivity at a temperature exceeding
      30K, of chemical formula or composition

10    $Mg_{1-x}X_xB_2$, where $0<x\leq0.5$ and X is Ca, Be, Al, Li, Zn, Cu, Ni Cr, Ti, Zr, Gd, W,
      Mo or any combination thereof.

2.   A compound according to claim1 wherein $0<x\leq0.3$.

3.   A compound according to claim 1 wherein $0<x<0.1$.

4.   A compound according to claim 1 wherein $0<x<0.08$.

15   5.   A compound according to any one of claims 1 to 4 wherein X is Al, Cu, Zn, or a
      combination thereof.

6.   An elongate superconductive electrical conductor comprising a superconductor of
      chemical formula or composition $Mg_{1-x}X_xB_2$, where $0\leq x\leq0.5$ and X is Ca, Be, Al,
      Li Zn, Cu, Ni Cr, Ti, Zr, Gd, W, Mo, or any combination thereof.

20   7.   A conductor according to claim6 wherein $0<x\leq0.3$.

8.   A conductor according to claim 6 wherein $0<x<0.1$.

9.   A conductor according to claim 6 wherein $0<x<0.08$.

10.   A conductor according to any one of claims 6 to 9 wherein X is Al, Cu, Zn or a
      combination thereof.

25   11.   A conductor according to any one of claims 6 to 10 wherein the superconductor is
      composed of particles which have been sintered together.

12.   A method of forming an electrical conductor including the steps of compacting
      within an elongate metal container particles of a superconductor of chemical
      formula or composition $Mg_{1-x}X_xB_2$, where $0\leq x\leq0.5$ and X is Ca, Be, Al, Li Zn,

30   Cu, Ni Cr, Ti, Zr, Gd, W, or Mo, or any combination thereof.

13.   A method of forming a conductor including the steps of mixing together and
      reacting precursor materials to form a superconductor of chemical formula or
      composition $Mg_{1-x}X_xB_2$, where $0\leq x\leq0.5$ and X is Ca, Be, Al, Li Zn, Cu, Ni Cr, Ti,
      Zr, Gd, W, Mo, or any combination thereof.

35   14.   A method of forming a conductor according to any one of claims 13 to 19
      including intimately mixing particles of the precursor materials and compacting the

5   precursor materials into and reacting the precursor materials in an elongate metal container.

15. A method of forming a conductor according to claim 13 or claim 14 wherein the precursor materials include elemental boron and elemental magnesium.

16. A method of forming a conductor according to claim 14 or claim 15 including

10   heating the precursor materials to a reaction temperature sufficient to vaporize the magnesium precursor to react with the boron precursor in a gas-solid reaction.

17. A method of forming a conductor according to claim 15 including providing an inert layer between the superconductor compound or precursor materials and the interior surface of the metal container.

15   18. A method of forming a conductor according to claim 17 wherein the inert layer is a layer of boron nitride.

19. A method of forming a conductor according to any one of claims 14 to 18 including placing the precursor materials within the elongate metal container such that the boron precursor material is substantially surrounded by the magnesium

20   precursor material.

20. A method of forming a conductor according to any one of claims 12 to 19 including heating to react the precursor materials to a temperature between about 400°C and about 950°C.

21. A method of forming a conductor according to any one of claims 13 to 19

25   including intimately mixing the precursor materials as particles of average particle size less than one micron prior to heating and reacting the precursor materials.

22. A method of forming a conductor according to claim 21 including mixing the precursor materials together so as to form an alloy of precursor metals.

23. A method of forming a conductor according to either one of claims 21 and 22

30   including heating and reacting the precursor materials at a temperature in the range about 400°C to about 750°C.

24. A method of forming a conductor according to any one of claims 21 to 23 wherein the metal container is formed from Cu, Al, or an Al alloy.

25. A method of forming a conductor according to any one of claims 12 to 24

35   including subjecting the elongate metal container containing the precursor

5   materials or an elongate component formed of an alloy of the precursor materials to
       mechanical deformation to densify the precursor material.

26.   A method of forming a conductor according to claim 25 wherein the mechanical
       deformation includes further elongating the metal container or alloy component to
       reduce the cross-sectional dimension thereof and further compact the material
10   therein.

27.   A method of forming a conductor according to either one of claims 25 and 26
       including heating the metal container or alloy component while subjecting it to
       mechanical deformation to assist in densifying the material.

28.   A method of forming a conductor according to any one of claims 13 to 27
15   comprising the step of including particles of a fluxpinning-effective non-
       superconducting material in the superconductor.

29.   A method of forming a conductor according to any one of claims 12 to 28
       including carrying out a heat treatment of the superconductor to precipitate borides
       of the substituent metal X from the superconductor.

20 30.   A method according to any one of claims 12 to 29 including heating the metal
       container to sinter particles of the superconductor together.

31.   A method of forming an electrical conductor including the steps of :
       intimately mixing at the sub-micron level particles of a magnesium precursor
       material and a boron precursor material and a precursor material which is a source
25   of Ca, Be, AL, Li, Zn, CU, Ni, Cr, Ti, ZR, Gd, W, Mo or any combination thereof,
       compacting the precursor materials within an elongate metal tube, subjecting the
       metal tube to mechanical deformation to reduce the cross-sectional dimension
       thereof and further compact the materials therein, and heating the metal container
       to react the precursor materials to form a superconductor of chemical formula or
30   composition $Mg_{1-x}X_xB_2$, where $0 \leq x \leq 0.5$ and X is Ca, Be, Al, Li Zn, Cu, Ni Cr, Ti,
       Zr, Gd, W, or Mo, or any combination thereof, where x is between $0 \leq x \leq 0.5$ and to
       precipitate fluxpinning – effective borides of the substituent metal X distributed
       within the resultant superconductor material.

32.   A method of forming an electrical conductor including the steps of :
35   intimately mixing at the sub-micron level particles of a magnesium precursor
       material and a boron precursor material and a precursor material which is a source

5   of Ca, Be, AL, Li, Zn, CU, Ni, Cr, Ti, ZR, Gd, W, Mo or any combination thereof, subjecting the elongate alloy component to mechanical deformation to reduce the cross-sectional dimension thereof, and heating the alloy component to react the precursor materials to form a superconductor of chemical formula or composition $Mg_{1-x}X_xB_2$, where $0 \leq x \leq 0.5$ and X is Ca, Be, Al, Li Zn, Cu, Ni Cr, Ti, Zr, Gd, W,

10   or Mo, or any combination thereof, where x is between $0 \leq x \leq 0.5$ and to precipitate fluxpinning – effective borides of the substituent metal X distributed within the resultant superconductor material.

33.   A method according to claim 31 or claim 32 wherein X is Al, Cu, Zn or a combination thereof.

15   34.   A method of forming a conductor according to anyone of claims 31 to 33 wherein the precursor materials include elemental boron and elemental magnesium.

35.   A method of forming a conductor according to cliam 31 including heating the metal container precursor materials to a reaction temperature sufficient to vaporize the magnesium precursor to react with the boron precursor in a gas-solid reaction.

20   36.   A method of forming a conductor according to any one of claims 31 to 34 including heating the metal container or alloy component to react the precursor materials to a temperature in the range about 400°C to about 750°C.

37.   A method of forming a conductor according to claim 31 wherein the metal container is formed from Cu, Al, or an Al alloy.
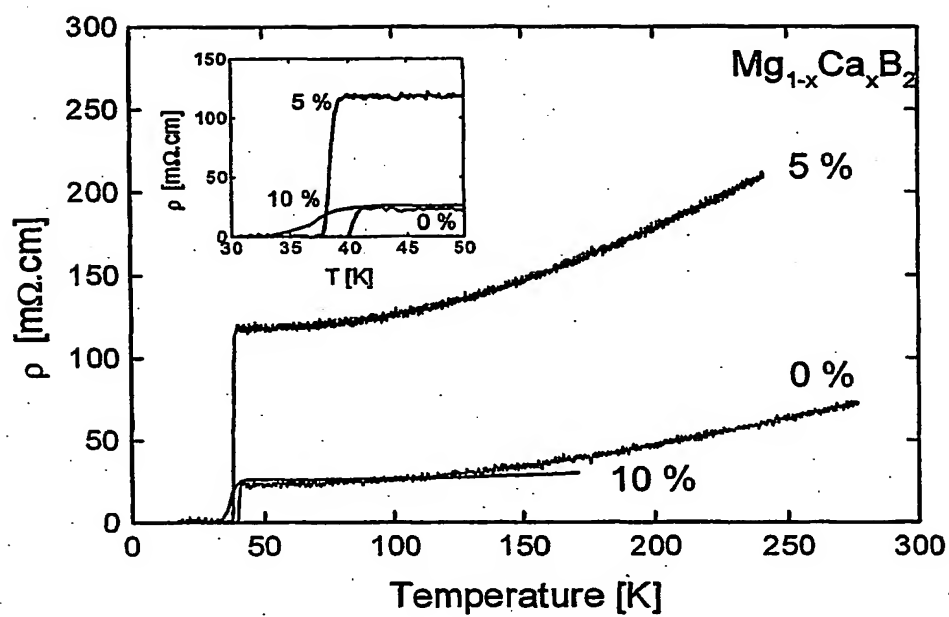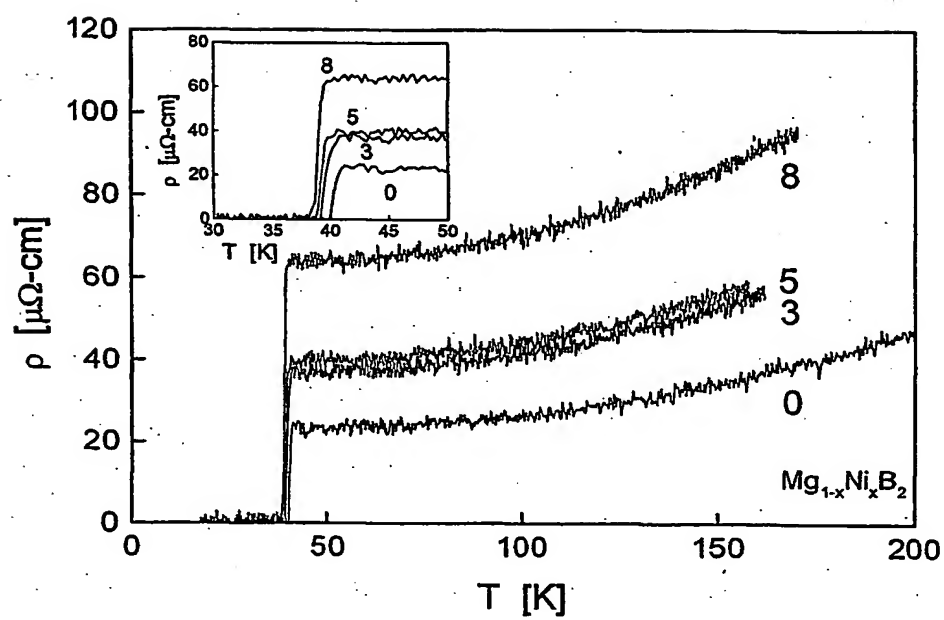
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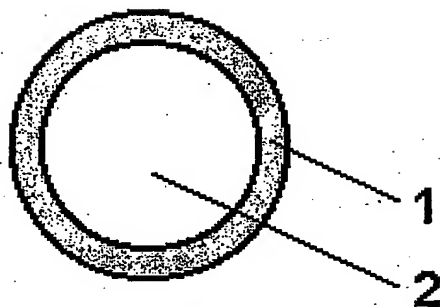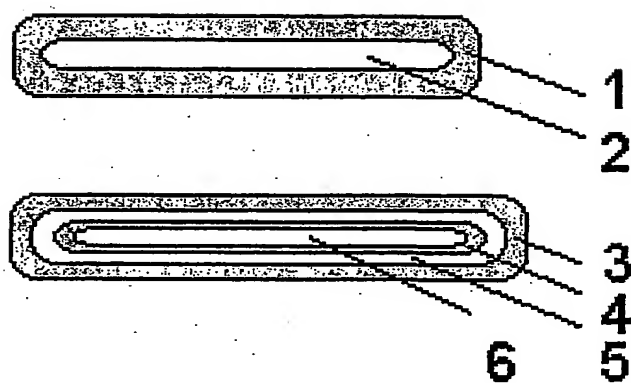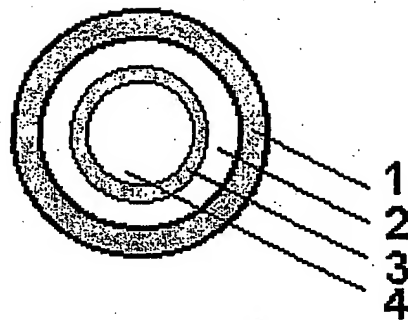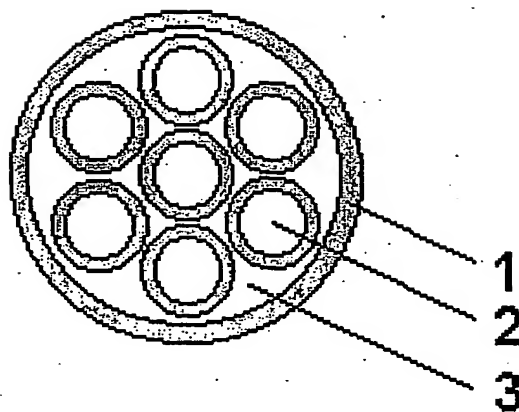
Figure 1

Figure 2

Figure 3

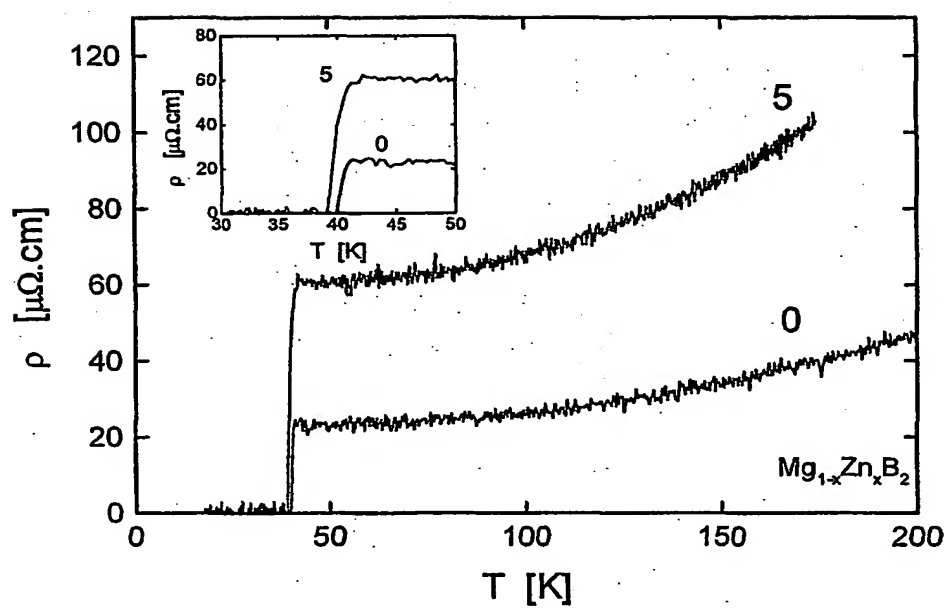**Figure 4**

Figure 5
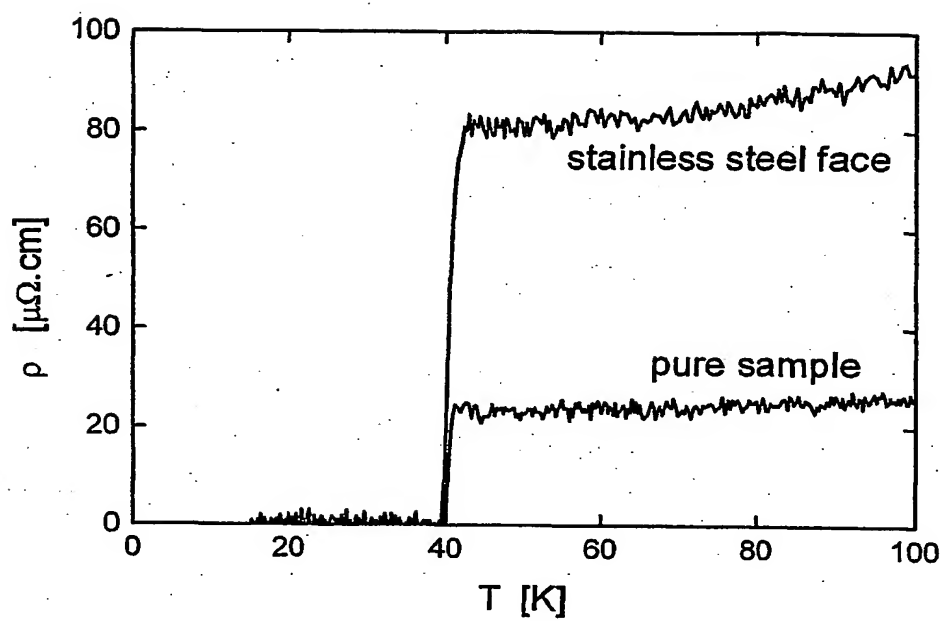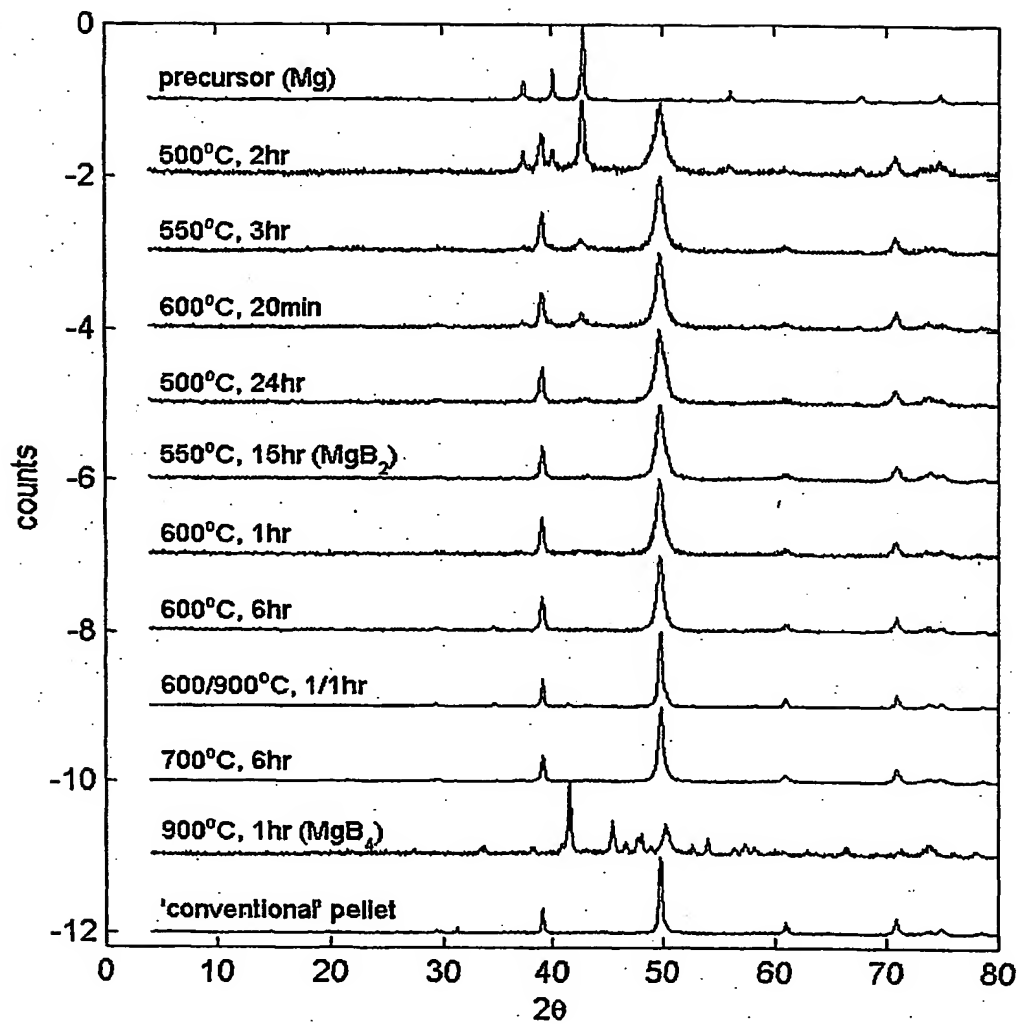
Figure 6

Figure 7

Figure 8

Figure 9

Figure 10
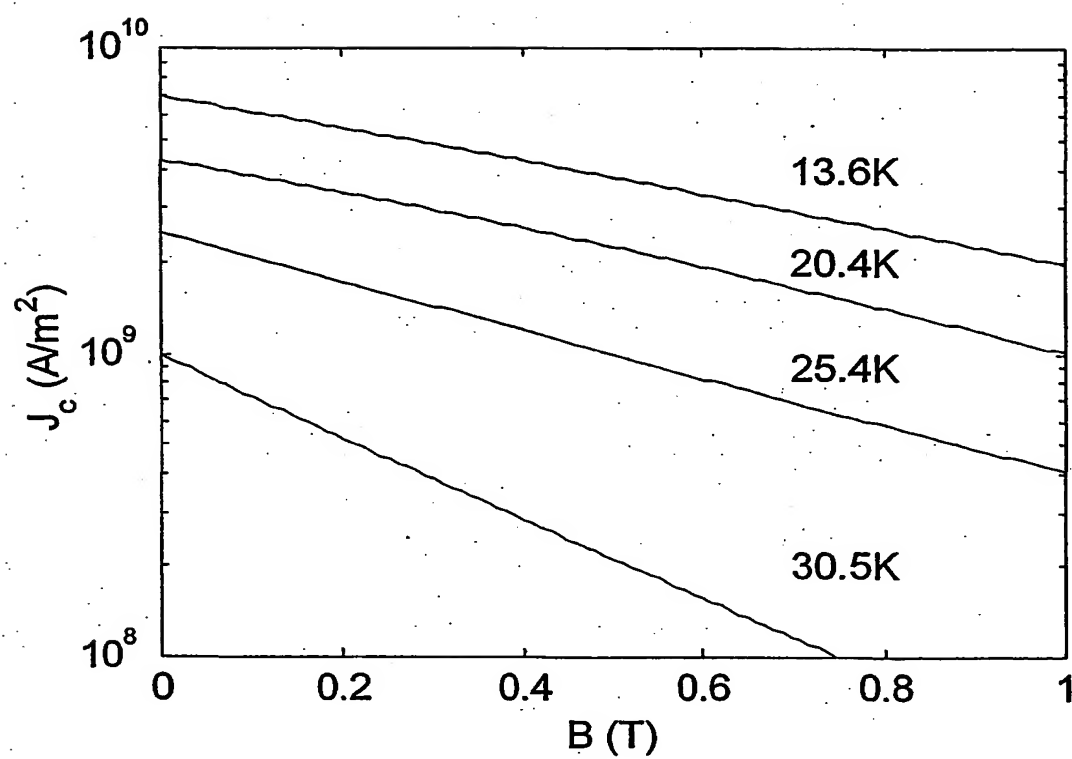
Figure 11

A.	CLASSIFICATION OF SUBJECT MATTER

Int.Cl^7:   H01B 12/00, H01L 39/12, C04B 35/58, C22C 29/14

According to International Patent Classification (IPC) or to both national classification and IPC

B.	FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl^7:   H01B 12/00, H01L 39/12, C04B 35/58, C22C 29/14

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

(1) DWPI: superconduct+ and (boride? or boron) and magnesium, with *Int.Cl^7* marks as above and additional search terms; and (2) Internet search on <URL: http://arxiv.org>

C.	DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	SLUSKY et al. "Loss of superconductivity and structural transition in $Mg_{1-x}Al_xB_2$" [online] 14 February 2001, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?102262>.	1-16,20-24 25-37
Y	CANFIELD et al. "Superconductivity in Dense MgB_2 Wires" [online] 15 February 2001, revised 17 February 2001, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?102289>.	25-37
X	SUZUKI et al. "Two-Dimensional σ-Hole Systems in Boron Layers: A First-Principles Study on $Mg_{1-x}Na_xB_2$ and $Mg_{1-x}Al_xB_2$" [online] 27 February 2001, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?102484>.	1-16

[X] Further documents are listed in the continuation of Box C	[ ] See patent family annex

*	Special categories of cited documents:		
"A"	document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search	Date of mailing of the international search report
7 June 2002	**1 3 JUN 2002**

Name and mailing address of the ISA/AU	Authorized officer
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C (Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	ZHAO et al. "Effect of Li doping on structure and superconducting transition temperature of $Mg_{1-x}Li_xB_2$" [online] 3 March 2001, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?0103077>.	1-4,6-9,12-16
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P, X	KAZAKOV et al. "Substitution effect of Zn and Cu in MgB_2 on T_c and structure" [online] 16 March 2001, revised 12 March 2002, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?0103350>.	1-14
P, A	CUNNINGHAM et al. "Synthesis and Processing of MgB_2 powders and wires" [online] 19 March 2001, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?103390>.	
P, X	LI et al. "Superconductivity and Aluminum Ordering in $Mg_{1-x}Al_xB_2$" [online] 18 April 2001, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?104320>.	1-5
P, A	GASPAROV et al. "Electron Transport in Diborides: Observation of Superconductivity in ZrB_2" [online] 18 April 2001, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?104323>.	
P, A	MEDVEDEVA et al. "Electric field gradients in s-, p- and d-metal diborides and the effect of pressure on the band structure and T_c in MgB_2" [online] 18 April 2001, revised 6 November 2001, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?0104346>.	
P, X	MEHL et al. "Effects of C, Cu and Be substitutions in superconducting MgB_2" [online] 27 April 2001, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?104548>.	1-4
P, X	MORITOMO et al. "Effects of transition metal doping in MgB_2 superconductor" [online] 30 April 2001, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?0104568>.	1-4
P, X	CIMBERLE et al. "Magnetic characterization of sintered MgB2 samples: effect of the substitution or 'doping' with Li Al and Si" [online] 10 May 2001, revised 13 May 2001, revised 7 June 2001, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?0105212>.	1-16
P, A	PAPAVASSILIOU et al. "^{11}B NMR detection of the magnetic field distribution in the mixed superconducting state of MgB_2" [online] 24 July 2001, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?0107511>.	
P, X	BUZEA et al. "Review of superconducting properties of MgB_2" [online] 16 August 2001, revised 26 September 2001, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?0108265>.	1-37

C (Continuation)	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	GLOWACKI et al. "Superconducting properties of the powder-in-tube Cu=Mg-B and Ag-Mg-B wires" [online] 5 September 2001, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?109085>.	1-37
P, X	BARABASH et al. "Structural and Superconducting Transitions in $Mg_{1-x}Al_xB_2$" [online] 21 November 2001, revised 26 February 2002, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?0111392>.	1-5
P, X	JOSEPH et al. "Effects of Disorder in $Mg_{1-x}Ta_xB_2$ Alloys using Coherent-Potential Approximation" [online] 8 January 2002, revised 19 February 2002, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?0201094>.	1-5
P, X	SOLTANIAN et al. "Improvement of critical current density in Cu/MgB_2 and Ag/MgB_2 superconducting wires using the fast formation method" [online] 15 January 2002, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?0201261>.	1-37
P, X	LIU et al. "X-ray photoemission study of polycrystalline $Mg_{1-x}Al_xB_2$" [online] 1 February 2002, revised 5 February 2002, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?0202007>.	1-5
P, X	SINGH et al. "Theoretical Study of Magnetism and Superconductivity in $3d$ Transition-Metal-MgB_2 Alloys" [online] 17 February 2002, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?0202285>.	1-5
P, X	AHN et al. "Structural and superconducting properties of $MgB_{2-x}Be_x$" [online] 23 February 2002, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?0202415>.	1-4
T	DE LA PEÑA et al. "Effects of Al doping on the structural and electronic properties of $Mg_{1-x}Al_xB_2$" [online] 22 March 2002, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?0203003>.	
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T	MARGADONNA et al. "Crystal Structure of $Mg_{1-x}Al_xB_2$ superconductors near $x \approx 0.5$" [online] 31 March 2002, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?>0204015>.	
T	SCHUPPLER et al. "Electronic structure of single-crystalline $Mg_xAl_{1-x}B_2$" [online] 10 mAY 2002, [retrieved on 2002-06-06]. Retrieved from the Internet <URL: http://arxiv.org/abs/cond-mat?0205230>.	